High Pressure Study of $Co_2(CO)_6(XPh_3)_2$ (X=As,P) Phase Transitions via SXRD

Nicola Casati, Piero Macchi, Angelo Sironi, *Department of Structural chemistry and Inorganic Stereochemistry, Università degli Studi di Milano, Italy.* E-mail: nicasati@istm.cnr.it

High Pressure (HP) is a powerful tool to induce structural modifications and phase transition in crystals. Molecular crystals, in particular, may show large variations both in intermolecular and intramolecular geometrical parameters but, up to now, have been subject to few studies.

The $M_2(CO)_{10}$ (M=Mn,Re) dimers have been suggested to undergo a staggered to eclipsed conformational rearrangement of the equatorial carbonyls, but their crystals do not survive this phase transition. With the aim of elucidating this behaviour we report the structural characterisations of the related $Co_2(CO)_6(XPh_3)_2$ (X=As,P) species, which are known to undergo a second order phase transition at low T[1], at different pressures (up to 46 kbar).

We confirm that a staggered to almost eclipsed conformational rearrangement takes place in both cases. This is accompanied by significant variations of most inter and intramolecular parameters. The HP behaviour is similar but larger than that observed on cooling, allowing to observe previously undetected variations of the intramolecular parameters.

[1] Macchi P., Garlaschelli L., Martinengo S., Sironi A., *Inorg. Chem.,* 1998, **37**, 6263.

Keywords: high pressure structure determination, phase transitions crystals characterization, molecular structure